

Modelling the Rheology of Polyvinyl Acetate Adhesive

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The shear stress, σ , and shear-rate, $\dot{\epsilon}$, experienced by polyvinyl acetate adhesive (PVA glue) as it is sheared in a rotational viscometer are measured at 21 temperatures, T , to investigate its flow properties. These data are fitted with various rheological models. The best fits, determined by χ^2 analysis, are the Herschel-Bulkley and Power Law models. From these models, the flow index n is found to be $n < 1$ for all T , hence PVA glue is categorised as a shear-thinning fluid. These data also reveal an intriguing $\eta - T$ phenomenon. For constant $\dot{\epsilon}$, η decreases with T , as is expected of liquids, only to increase significantly at $T \approx 55.0^\circ\text{C}$ and decrease again at $T \approx 65.0^\circ\text{C}$. This phenomenon is compared to similar behaviour in starch; its significance in terms of thermal gelation and intermolecular bonds is discussed. η 's time dependence is also investigated; a polynomial model is proposed to describe this relationship. The suitability of all models is discussed in terms of errors, χ^2 and normalised residuals.

I Introduction

The absolute viscosity of a fluid, η , is a measure of its internal friction. For a Newtonian fluid, an applied shear stress, σ , results in flow with a proportional shear-rate, $\dot{\epsilon}$. The constant of proportionality is η ; this simple relationship is as follows:

$$\sigma = \eta \dot{\epsilon}, \quad (1)$$

However, for non-Newtonian fluids, η can vary depending on factors such as time, t , and $\dot{\epsilon}$. Shear-thinning fluids become less viscous with increased $\dot{\epsilon}$; the opposite is true of shear-thickening fluids (also known as dilatant fluids). Shear-rate dependent η can be given by a power law:

$$\eta(\dot{\epsilon}) = k \dot{\epsilon}^{n-1}, \quad (2)$$

k is the consistency index and n is the flow behaviour index, which defines the shear-rate dependence of a fluid. Shear-thinning, Newtonian and shear-thickening liquids have $n < 1$, $n = 1$ and $n > 1$ respectively [1]. A fluid at a given temperature has its own characteristic values of these indices.

For liquids, it is established that η generally decreases as temperature increases. The exact relationship varies between materials.

The $\sigma - \dot{\epsilon}$ relationship for polymeric fluids can often be described using the Power Law model:

$$\sigma = k \dot{\epsilon}^n. \quad (3)$$

In this work, we investigate whether this is an appropriate model for the rheology of PVA glue, a water-based emulsion of the synthetic polymer polyvinyl acetate (not to be confused with polyvinyl alcohol). If it is, we use it to determine PVA glue's shear-rate dependence. Dilatant behaviour is commonly exhibited by mixtures, so $n > 1$ is expected [2]. We also investigate other potential models, including the Bingham model:

$$\sigma = \sigma_0 + \eta \dot{\epsilon}, \quad (4)$$

the Herschel-Bulkley model (a modification of the Power Law model):

$$\sigma = \sigma_0 + k \dot{\epsilon}^n \quad (5)$$

and the Casson model:

$$\sqrt{\sigma} = \sqrt{\sigma_0} + \sqrt{\eta \dot{\epsilon}}. \quad (6)$$

σ_0 is the yield stress, the stress required for flow to start. k and n are as already defined [3]. We also model the T -dependence of η and investigate PVA glue's possible thixotropic properties, i.e. the effects of t on η .

II Methods

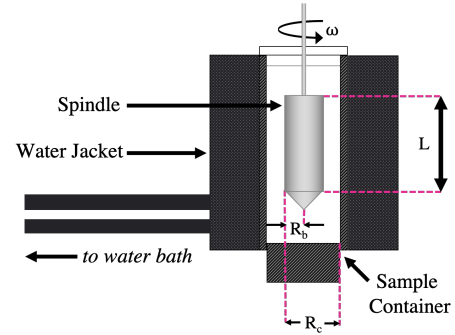


Figure 1: Diagram to show a section of the viscometer including the SC4-27 spindle, sample container and water jacket; R_b is the radius of the spindle and R_c is the radius of the container, whilst L is the effective length of the spindle. The spindle is attached to the motorised component of the viscometer, not shown here.

All measurements in this work are made using a Brookfield viscometer and its complementary software package Rheocalc. A cylinder filled with PVA glue is inserted into the water jacket cavity, kept at a stable temperature T (with precision $\pm 0.1^\circ\text{C}$). A rotating spindle is submerged in the sample, and a lid placed to reduce heat loss and sample evaporation (see figure 1). For user-specified T , spindle rotation speeds ω and end conditions (in this case a maximum percentage torque, M) as stated below, the viscometer measures σ , $\dot{\epsilon}$, and M , based on ω , R_c , R_b , and L (defined in figure 1). Assuming the container and spindle are co-centric cylinders, $\dot{\epsilon}$ and σ are:

$$\dot{\epsilon} = \frac{2R_c^2}{R_c^2 - R_b^2} \omega, \quad (7)$$

$$\sigma = \frac{M}{2\pi R_b^2 L}. \quad (8)$$

η can then be found using equation 1 [3].

For ascending ω , σ , $\dot{\epsilon}$ and η were measured at 15 s intervals to allow the spindle to stabilise at each successive ω . Stable measurements can only be made for $(5.0 \pm 0.1)\% < M < (95.0 \pm 0.1)\%$, so ω were selected accordingly. This process was repeated for water jacket temperatures $15.0^\circ\text{C} \leq T \leq 75.0^\circ\text{C}$. To reduce sample-sample variation, the same amount of glue, weighed to be (13.6 ± 0.1) g, was used in each repeat.

III Results

III.1 $\sigma - \dot{\epsilon}$ Models

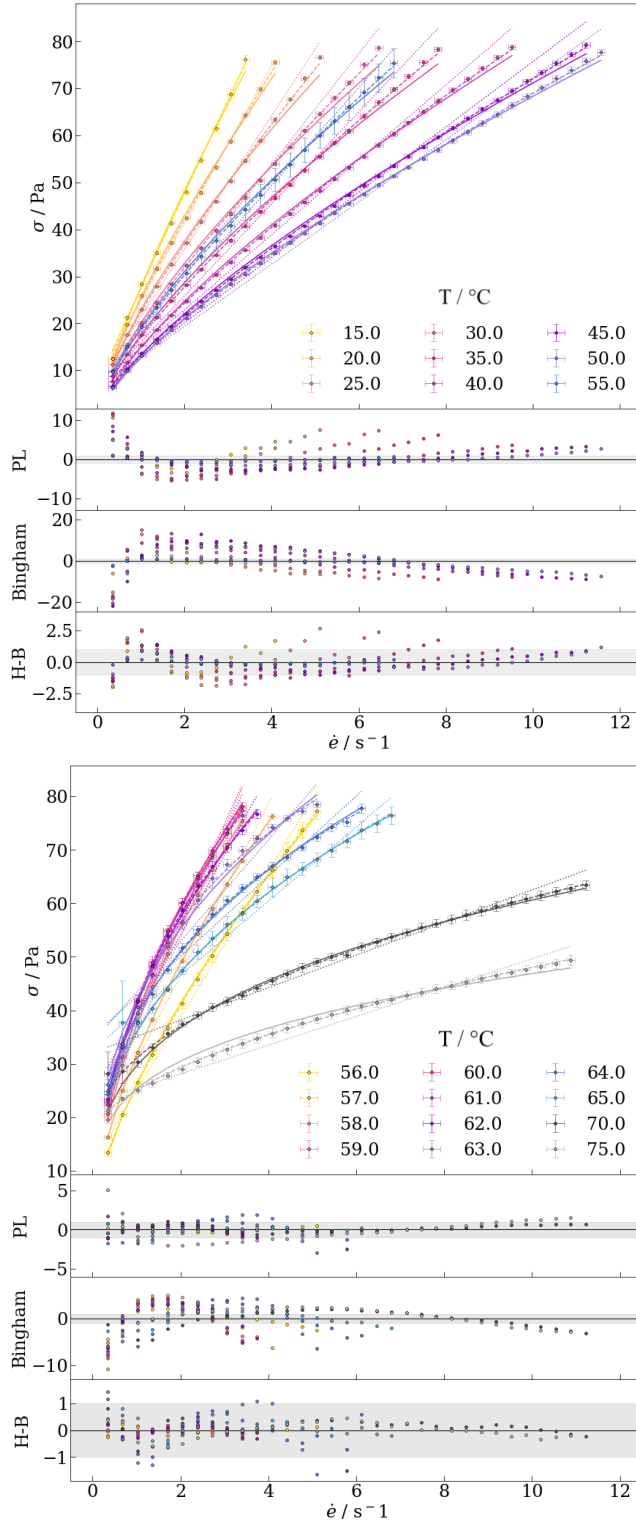


Figure 2: $\dot{\epsilon}$ - σ profiles for PVA glue. The top plot (i) and lower plot (ii) show lower and higher T respectively. The solid, dashed and dotted fits are PL, H-B and B respectively. Normalised residuals are plotted at all T for each of the 3 models. The majority of the residual data lie within the shaded $\pm 1\text{-}\sigma$ region of the H-B residual on both (i) and (ii), and within this region of the PL residual on (i). More than $\frac{2}{3}$ of points in this region implies a good fit. However, some residuals show clear structure, e.g. $T = 56.0^\circ\text{C}$ in the H-B subplot, implying an additional term should be added to the model. The quality of all the fits cannot be confirmed by inspection, so is further explored via χ^2 analysis. It should be noted that some error bars overlap. σ error bars are of the order 10^{-2} and have been scaled by a factor of 5.

$T/^\circ\text{C}$	χ^2_ν				Fit
	PL	H-B	C	B	
15.0	3.76	1.34	N/A	1.94	H-B
20.0	10.5	1.90	N/A	6.67	H-B
25.0	26.8	3.01	N/A	57.6	H-B
30.0	25.2	2.07	N/A	70.2	H-B
35.0	18.5	1.18	N/A	63.2	H-B
40.0	7.59	0.599	N/A	44.9	H-B
45.0	6.95	0.451	N/A	61.8	H-B
50.0	2.47	0.224	N/A	34.7	PL
55.0	0.207	0.0204	N/A	0.810	B
56.0	0.158	0.0156	N/A	4.01	PL
57.0	0.0749	0.0346	N/A	28.0	PL
58.0	0.0343	0.00325	N/A	10.9	PL
59.0	0.224	0.00969	N/A	21.4	PL
60.0	0.410	0.0329	N/A	20.0	PL
61.0	0.476	0.0523	N/A	15.9	PL
62.0	0.478	0.0751	N/A	11.7	PL
63.0	2.56	1.08	4.43	17.1	H-B
64.0	0.839	0.433	2.11	12.3	PL
65.0	0.133	0.120	0.147	2.07	B
70.0	0.574	0.189	0.205	3.84	PL
75.0	2.38	0.0967	0.159	4.57	PL

Table 1: χ^2_ν values for the Power Law (PL), Herschel-Bulkley (H-B), Casson (C) and Bingham (B) models. Not all T could be fitted with C due to negative constants. Fit column shows best fit as determined from χ^2_ν .

The mean of the 3 repeat σ - $\dot{\epsilon}$ data sets were taken, giving one σ - $\dot{\epsilon}$ set, for each T . These data were then fitted to the models described in section I using `scipy.optimize.minimize`. χ^2_ν values were calculated to investigate quality of the calculated fits, as shown in table 1. [4] states that for a good fit, $\chi^2_\nu \approx 1$. A poor fit is defined as $\chi^2_\nu > 3$ or $\chi^2_\nu \ll 1$. Models yielding values in these ranges were deemed unsuitable. This is further discussed in section IV.

$T/^\circ\text{C}$	$n \pm \alpha_n$	$(k \pm \alpha_k) / \text{Pa.s}^n$	$(\sigma_0 \pm \alpha_{\sigma_0}) / \text{Pa}$
15.0	0.95 ± 0.08	21 ± 3	6 ± 3
20.0	0.8 ± 0.05	20 ± 2	5 ± 2
25.0	0.82 ± 0.03	19 ± 1	4 ± 1
30.0	0.81 ± 0.03	16.4 ± 0.9	3 ± 1
35.0	0.80 ± 0.02	14.3 ± 0.6	2.8 ± 0.8
40.0	0.80 ± 0.01	12.6 ± 0.4	2.5 ± 0.6
45.0	0.789 ± 0.008	11.4 ± 0.3	2.0 ± 0.3
50.0	0.73 ± 0.06	12.695 ± 0.002	N/A
56.0	0.66 ± 0.01	26.2 ± 0.3	N/A
57.0	0.623 ± 0.005	31.7 ± 0.2	N/A
58.0	0.581 ± 0.009	37.1 ± 0.3	N/A
59.0	0.566 ± 0.006	39.0 ± 0.2	N/A
60.0	0.536 ± 0.007	40.8 ± 0.2	N/A
61.0	0.512 ± 0.008	41.3 ± 0.3	N/A
62.0	0.48 ± 0.01	41.1 ± 0.4	N/A
63.0	0.18 ± 0.08	100 ± 600	100 ± 600
64.0	0.381 ± 0.006	39.1 ± 0.3	N/A
70.0	0.311 ± 0.005	29.6 ± 0.3	N/A
75.0	0.267 ± 0.004	25.3 ± 0.2	N/A

Table 2: n and k values for the Power Law (PL) and Herschel-Bulkley (H-B) models; models are distinguishable by PL's lack of σ_0 values.

For all Power Law and Herschel-Bulkley obeying data sets, the constant n can be found. Hence we determine the shear-dependence of PVA glue. As seen in table 2, all $n \pm \alpha_n > 1$; therefore PVA glue exhibits shear-thinning properties.

III.2 $\eta - T$ Dependence

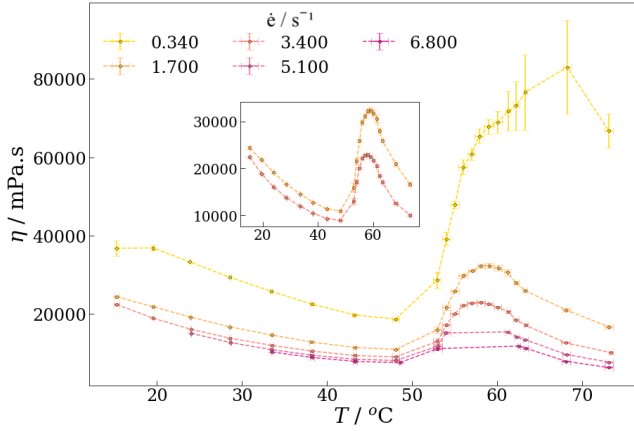


Figure 3: $\eta - T$ profiles for PVA glue for various constant $\dot{\epsilon}$. Points are connected for clarity but no model is fitted. For lower $\dot{\epsilon}$, the η increase at approximately 55°C is far more dramatic. Inset shows moderate $\dot{\epsilon}$ values to better display the curve. Error bars are not all visible. The smallest η and T error bars are of the order of 10 and 10^{-2} respectively. All errors in $\dot{\epsilon}$ are ± 0.02 .

The data in figure 2 yield another interesting result; though for increasing T , the $\sigma - \dot{\epsilon}$ gradient (i.e. η) tends to decrease, this relationship breaks down for a critical region $55.0^\circ\text{C} \leq T \leq 65.0^\circ\text{C}$. By plotting η against the temperature of the glue at various constant $\dot{\epsilon}$ we investigate this further (figure 3).

PVA glue was also heated from room temperature to 75.0°C in a glass beaker on a hotplate to allow observation of the glue, with a magnetic stirrer to aid in even distribution of heat. The consistency of the glue went through an obvious change, not just in viscosity, but also in observed texture, in the critical region. Its opaque white colour broke down into translucent and opaque regions. Potential reasons for this are explored in section IV.

III.3 $\eta - t$ Dependence

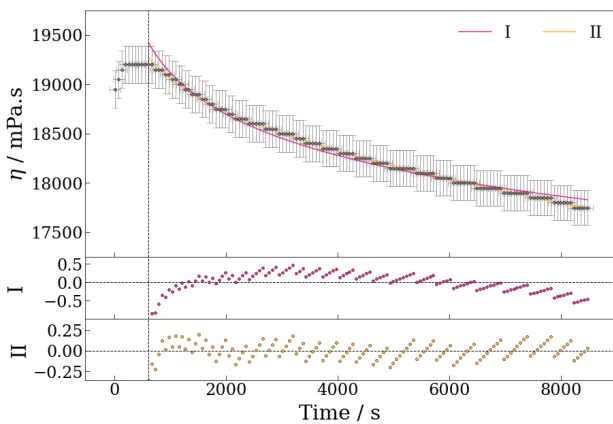


Figure 4: $\eta - t$ profile for $\omega = (5.00 \pm 0.01)$ RPM at glue temperature $T = 24.5^\circ\text{C}$. The lines shown are the fits I and II as determined by χ^2 analysis. t error bars ($\pm 10^{-2}$) are scaled by a factor of 100 for visibility. Only the decay curve has been modelled. The normalised residuals all lie within $1-\sigma$, and II lacks structure, implying a good fit. However, I follow a defined curve, suggesting an additional term should be incorporated into the model.

As shown in figure 4, η decreased non-linearly over time. By inspection, two fits were chosen for testing, both polynomial. A Power Law fit I with an added constant gives $\chi_\nu^2 = 0.0779$. This is poor, much less than 1. An alternative polynomial fit II with an added first order term gives $\chi_\nu^2 = 0.00999$, even smaller. Despite both fits being poor by definition, II is the preferred of these two fits due to its lack of residual structure:

$$\eta = at^b + ct \quad (9)$$

with $a = 22000 \pm 100$, $b = -0.0200 \pm 0.0007$ and $c = -0.0683 \pm 0.003$.

IV Discussion

Literature values of η or other constants for PVA glue are not readily available. We therefore focus not on the comparison of our numerical results with known values, but on deriving what we can about the nature of PVA glue from our results and applying fits to our data. Note that laminar flow, as opposed to turbulent, has been assumed for all data.

IV.1 $\sigma - \dot{\epsilon}$ Models

Overall, Power Law based models dominated, with cooler temperatures following the Herschel-Bulkley model and higher temperatures fitting the simpler Power Law model. However, although not poor, these models were not always good fits, as is evident from the values in table 1. There is also some polynomial structure in the H-B and PL normalised residual plots for most T .

The Casson model was overwhelmingly unsuitable, with the majority T values not yielding a χ_ν^2 at all. χ_ν^2 for those that did generally implied a poor fit.

The Bingham model was not expected to be suitable as it describes Newtonian flow, unlikely for a complex fluid such as PVA glue. Generally this is reflected in the normalised residuals, with very few points lying in the $1 \pm \sigma$ region, and clear structure in the residuals for all T . However, for 55.0°C and 65.0°C , the best fit was the Bingham model. This is of interest as these are the temperatures at which the $\eta - T$ profiles dramatically change in shape, i.e. where η begins to increase and then where it decreases again. The Bingham model was also found to be suitable (though was not the best fit) at $T = 15.0^\circ\text{C}$. n is also close to 1 at this T ; $n = 1$ indicates a fluid is Newtonian. This may be significant as this T was where the glue was first sheared, introducing the possibility that the shear behaviour of PVA glue changes over time or prolonged stirring. However, these may all just be anomalous fits, coincidentally at critical points. More repeats could confirm or deny this.

Values of $\chi_\nu^2 \ll 1$ could be the result of underestimated errors. However, not all data have χ_ν^2 in this range and there are larger error bars on some data points implying large sample-sample variation. Particularly noticeably, the initial points at $T = 70.0^\circ\text{C}$ and $T = 65.0^\circ\text{C}$ have larger σ errors. A likely cause of this is the spindle not being straight and wobbling its way into a vertical position as it began to rotate. The entire $T = 55.0^\circ\text{C}$ and $T = 65.0^\circ\text{C}$ data sets has larger σ errors, too. This could also be due to spindle instability, this time due to the sudden increase and decrease in η that occur respectively at these temperatures (see figure 3). These errors could be avoided by running the viscometer for longer

before collecting data to allow the spindle to become coaxial with the sample cylinder. More accurate results and errors could also have been attained if more repeat data sets had been taken. Unfortunately due to the nature of the equipment and experiment there was not time for this.

The values of n at different T categorise PVA glue as a shear-thinning fluid, and there is positive correlation between n and T . This shows increasingly non-Newtonian flow with increasing T . This is also the case for fruit jams at $20 < T < 40^\circ\text{C}$; they too follow a Power Law $\sigma - \dot{\epsilon}$ relationship and exhibit shear-thinning behaviour. Though superficially different, both jam and PVA glue are complex fluids consisting of a suspended solid particles and long molecules, which may account for their similar behaviour [5]. Though errors in the fit parameters are generally approximately $\pm 10\%$, there is one case, $T = 63.0^\circ\text{C}$, with errors in k and σ_0 of $\pm 600\%$. By inspection of figure 2, many points do not lie on the H-B fit, despite χ^2_ν declaring it the best fit. A different fit might yield more accurate parameters. Fits not tested include the Steiger-Ory and NCA/CMA Casson models. NCA/CMA Casson is a modification of the Casson model involving additional factors and so is likely unsuitable, but Steiger-Ory is a polynomial model specifically for shear-thinning fluid so may have been more representative of the glue's behaviour [6].

It is important to note that the water jacket temperature is not the same as the temperature of the glue. The inside of the sample tube, even when left to stabilise for 15 minutes as advised in [3], never reached T , and instead remained approximately 2°C lower. This is considered in the η - T profiles, where T is taken as the glue temperature. However, all other T are the water jacket temperature and are assumed to be constant. In reality, again despite leaving the sample to stabilise for 15 minutes, temperature fluctuated fractionally. The viscometer in general assumes implausibly high precision; this does not affect most of this work, but as errors in $\dot{\epsilon}$ was calculated from instrument precision (see errors appendix), they may be unrealistically small.

IV.2 $\eta - T$ Profiles

Though no literature comparison can be found for PVA glue, when starch solution is heated, a similar η peak is present in the $\eta - T$ profile. In the case of starch solution, this is because at a critical temperature called the gelation temperature, the system is thermally energetic enough for the hydrogen bonds within its structure to be overcome, allowing water to penetrate the crystals of starch. This causes them to swell, which dramatically increases η for the solution. However, as stirring continues, these structures "burst", and η decreases [7]. It is likely that PVA glue follows this trend for a similar reason; it too is a solution of polymers which interact via hydrogen bonding [2]. Indeed the change in opacity observed on the hotplate could be from the crystalline structure breaking down into dispersed PVA clusters. Whether or not this process is reversible was not investigated. Measurements for descending T as opposed to ascending could not be made due to lab time constraints and the nature of the equipment. However, as hydrogen bonding is a reversible process [2], we hypothesise that gelation, i.e. the initial increase in η , and the "bursting" are reversible.

There is the case of the $\dot{\epsilon} = 0.340 \text{ s}^{-1}$ curve where η increases

far more dramatically; this does however fit with the apparent trend of the peak η being approximately twice the starting η . Whether this is just a coincidence is uncertain. This data set also has much larger error bars than the others. This is down to large sample-sample variation. As this was the starting $\dot{\epsilon}$ for all T , there is a likelihood that the spindle was not fully stable, causing measurements of σ , and consequently η , to vary greatly between repeats.

IV.3 $\eta - t$ Dependence

A decrease in η over time categorises a fluid as thixotropic. This $\eta - t$ dependence is a common characteristic of multi-phase mixtures. As an emulsion, PVA glue belongs in this category of fluids [4]. However after careful consideration it was decided that the effects of this relationship our $\sigma - \dot{\epsilon}$ measurements were negligible. A decrease in η of 6.33% over a period of approximately 8000 s is sufficiently small that it needs not be taken into account in previous calculations, and we can still call PVA glue a shear-thinning fluid. Constant T has been assumed as all fluctuations were within the range of error in T .

The model chosen for $\eta - t$ is poor as it was invented from inspection. another contributor to the small value of χ^2_ν may be underestimated errors (the propagation of these is described in the Error Appendix on page 4). Only the decay curve has been modelled for simplicity. Reasons for the initial rise in η are unclear.

V Conclusions

PVA glue is found to be a shear-thinning fluid. The relationship between σ and $\dot{\epsilon}$ is best described using power laws models, with cooler temperatures favouring the Herschel-Bulkley model and higher temperatures favouring a simple Power Law with no additional constant. Though it is a liquid, the usual decrease in η with increased T does not apply to PVA glue for all T , thought to be due to changes in intermolecular bonding in the $55.0^\circ\text{C} \leq T \leq 65.0^\circ\text{C}$ region. There is not a significant $\eta - t$ dependence.

References

- [1] R. Jones, "Soft Condensed Matter", 3rd edition, Oxford University Press, UK (2004)
- [2] M. Alger, "Polymer Science Dictionary", 3rd edition, Springer, UK (2017)
- [3] Brookfield AMETEX, "More Solutions to Sticky Problems", Brookfield Engineering Laboratories, Inc., USA (2017)
- [4] I. Hughes and T. Hase, "Measurements and their Uncertainties", Oxford University Press, UK (2010)
- [5] J. Tiffany, International Journal of Ophthalmology, **15** : 6, 371 (1991)
- [6] E. Ivarez et al., International Journal of Food Properties, **9** : 1, 135 (2006)
- [7] "NPTEL :: Textile Engineering - Fabric Manufacture - I", <https://nptel.ac.in/courses/116102005/20> (accessed 19/03/19)

VI Error Appendix

VI.1 Measured Variables

The errors in T , M , t and the sample mass, α_T , α_M , α_t and α_m , were determined from the precision of the viscometer (and its built-in thermometer and clock) and the weighing balance respectively:

$$\alpha_T = 0.1 \quad (10)$$

$$\alpha_M = 0.1 \quad (11)$$

$$\alpha_t = 0.1 \quad (12)$$

$$\alpha_m = 0.1. \quad (13)$$

Values of T in this work are quoted without errors. This is in a deliberate effort to make the piece more easily readable. Their precision is always the same, the exception being T in the $\eta - T$ experiment, in which three different T were calculated from the mean of three data sets. Similarly, η in this experiment, and σ in the $\dot{\epsilon} - \sigma$ experiment, were also mean values. Therefore, α_T for this specific case, along with α_η and α_σ , were found as follows:

$$\alpha_Z = \frac{\sigma_N}{\sqrt{N}}. \quad (14)$$

This is standard error as seen in [4]. N is the number of measurements taken, and σ_N is the standard deviation. This is not to be confused with σ , stress. Z represents T , η or σ .

There is an exception for η in the $\eta - t$ experiment, where one data set was taken:

$$\alpha_\eta = 1\% \times \eta [3]. \quad (15)$$

$\dot{\epsilon}$ values were consistent throughout data sets and so no standard error could be calculated. From the precision of each measurement, ± 0.001 , and using the Pythagoras approach described in [4], error in $\dot{\epsilon}$ is as follows:

$$\alpha_{\dot{\epsilon}} = \sqrt{m \times (p)^2} \quad (16)$$

where m is the number of measurements and p is precision. Substituting values gives:

$$\alpha_{\dot{\epsilon}} = 0.02. \quad (17)$$

VI.2 Calculated Constants

The formal definition of χ^2 is that it is the sum of the normalised residuals squared. For example, for any of the $\sigma - \dot{\epsilon}$ data in this work:

$$\chi^2 = \sum_i \frac{(\sigma_i - \sigma(\dot{\epsilon}_i))^2}{\alpha_i^2}, \quad (18)$$

with σ_i , $\sigma_i(\dot{\epsilon}_i)$ and α_i as the i^{th} measurement of σ and its corresponding fit value and error [4].

χ_ν^2 and the errors in fit parameters n , k , σ_0 , a , b and c (α_n , α_k , α_{σ_0} , α_a , α_b and α_c) were calculated using Python. All errors are 1- σ .

For the two-parameter Power Law fit, errors were calculated via χ^2 minimisation. In this method, χ^2 is calculated for all

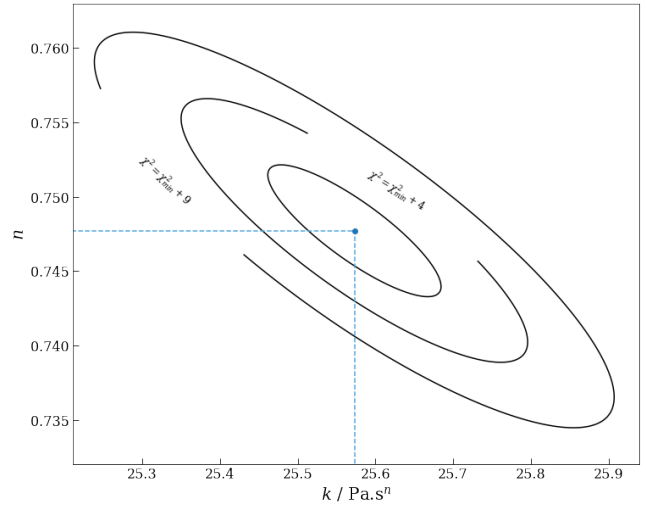


Figure 5: Example contour plot for the Power Law model at $T = 20.0^\circ\text{C}$. The central blue point represents χ_{min}^2 ; blue lines extend to the corresponding "best" n and k . The unlabelled inner line is the $\chi_{min}^2 + 1$ contour. The differences between the parameters at χ_{min}^2 and $\chi_{min}^2 + 4$ and χ_{min}^2 and $\chi_{min}^2 + 9$ are 2- σ and 3- σ errors respectively.

possible parameters and every data point. From these values a contour plot is produced (example given in figure 5). Each contour corresponds to parameters n and k with equal χ^2 ; the midpoint of these contours is χ_{min}^2 . The parameters of the best fit correspond to this point. The errors α_n and α_k are then calculated from the difference between each parameter in question at χ_{min}^2 and $\chi_{min}^2 + 1$.

χ_ν^2 , which describes the fit quality, is then calculated:

$$\chi_\nu^2 = \frac{\chi_{min}^2}{\nu}, \quad (19)$$

with ν , the number of degrees of freedom, defined as:

$$\nu = N - \bar{N}, \quad (20)$$

where N is the number of data points and \bar{N} is the number of parameters.

It is possible to calculate the errors in more than two parameters using χ^2 minimisation on multi-dimensional contour plots. However, when fits involving three parameters were introduced, the Python program, though successfully adapted to calculate the three parameters themselves (n , k and σ_0 and a , b and c) and the χ^2 values for these fits, could not be modified to propagate all three errors by this method.

Instead, a bootstrap method was employed. The method is as follows: using Python, a random set of numbers from the data set to be fit, of length N , was selected with replacement. The three parameters of the fit were determined for this random set by the same method as the two parameter fits described previously. This was repeated x times, where x is some number of the order of 10^3 . Errors were then determined by taking the standard deviation of all x of the calculated parameters. This was repeated for every three parameter fit. It is key that the random sets are taken with replacement so that they are not all identical to the original data set [4].